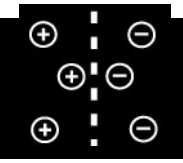
ECOLOGICALLY SAFE ION EXCHANGE TECHNOLOGIES



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The industrial application of ion exchange (IE) is growing. In many instances IE can successfully replace existing large scale industrial processes which do not satisfy modern ecological standards. To be competitive, IE technology should be highly efficient and ecologically safe. The general scheme of standard IE processes comprises several auxiliary operations (besides IE treatment), listed in **Table 1**. Several approaches have been applied to eliminate some of these auxiliary operations and to improve the efficiency and ecological safety of the process through significant savings of chemicals and energy and reduction of waste.

One of these approaches is based on the application of dual-temperature IE processes which exploit the different affinities of the resin towards ions to be separated at different temperatures. The main advantage of dual-temperature IE comes from avoiding the use of auxiliary reagents which are conventionally required to displace (strip) the ions to be separated from the resin phase and to regenerate the ion exchanger. This last stage is known to be the main source of waste in IE technology (Table 1). In dual-temperature IE, both stages can be combined in one through the use of a thermostripping procedure. This allows the exclusion of auxiliary operations 4 and 5. Hence, essentially reagentless and wasteless separation processes can be designed.

Another route to avoid auxiliary operations (e.g. numbers 2 and 3; Table 1) is based on a combination of IE conversion and the product concentration processes into one stage. Frontal IE chromatography and reverse frontal separation can be applied for this purpose. In certain instances, both of these IE separation techniques allow the concentration of the target substance to a level exceeding its solubility at a given temperature. Moreover, this supersaturated solution (SS) remains stable for a long period, while after leaving the column it crystallizes spontaneously. This allows the design of a nearly ideal process where a crystalline product is obtained directly after the IE treatment. The tailored application of this phenomenon (discovered by Muraviev and known as ion exchange isothermal supersaturation or IXISS) allows, in certain instances, for additional elimination of operations 4 and 5. Several examples of the tailored application of dual-temperature IE and IXISS effects to design ecologically safe IE technologies are given below.

IXISS-based IE Processes[1]

The tailored application of IXISS to design highly efficient IE technologies is based on the use of the IXISS-active stripping agents, which must meet the following requirements:

1. The IXISS-active eluent must on the one hand bear the desired counterion to combine the desorption of the product with the regeneration of the ion exchanger. On the other hand, it must also contain an appropriate co-ion to provide the formation of a stable SS of a low solubility compound (the product) and to shift the IE equilibrium in the system to the desired direction. For example, the IE reaction of displacement of a divalent metal ion, M_1^{2+} (e.g. Mg^{2+} or Ca^{2+}), by a monovalent one, M_2^{+} (e.g. Na^{+}), from a carboxylic cation exchanger can be written as follows:

$$(\text{R-COO}_-)_2M_1^{2+} + 2M_2^{+} \Leftrightarrow 2\text{R-COO}^-M_2^{+} + M_1^{2+} \qquad [1]$$

The equilibrium in reaction 1 is characterized by the equilibrium coefficient, $K_{M_2}^{M_1}$:

$$K_{M_2}^{M_1} = \frac{Q_{M_2}(C_{M_1})^{1/2}}{(Q_{M_1})^{1/2}C_{M_2}} \qquad [2]$$

where C and Q are the concentrations of ions in the solution and resin phases, respectively. For chloride media, $K_{M_2}^{M_1}$ is usually $\ll 1$. If reaction 1 proceeds in a carbonate medium, for example, when the resin in the M_1 form is treated with

[1] Adapted with permission from Muraviev D, Khamizov R, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. I. Synthesis of chlorine-free potassium fertilizers by an ion-exchange isothermal supersaturation technique. *Industrial Engineering and Chemistry Research* 37: 1950–1955.

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Table 1 Basic auxiliary operations of standard ion exchange process

No.	Operation	Consumption of		Wastes (approx. % of total)
		Energy	Chemicals	
1	Preparation of stock solution	Low	Low	Up to 5
2	Concentration of solution after IE treatment (e.g. by evaporation)	High	Low	
3	Recovery of purified product (e.g. by crystallization)	Medium	Low	Up to 5
4	Regeneration of ion exchanger and auxiliary chemicals for reuse	Low/medium	High	Up to 80
5	Neutralization of waste before their disposal	Low	High/medium	Up to 10

M_2 carbonate solution (C_o, mol dm^{-3}), it is coupled with the formation of M_1 carbonate, which can be described by the solubility product of M_1CO_3 ($L_{M_1CO_3}$), where:

$$L_{M_1CO_3} = C_{M_1^{2+}} C_{CO_3^{2-}} \quad [3]$$

If M_1CO_3 forms a stable SS, where it exists in an associated (molecular) form at a concentration C_M mol dm^{-3} exceeding γ times its solubility, C_S, at a given temperature, eqn [3] takes the following form:

$$L_{M_1CO_3} = C_{M_1^{2+}}(C_o - C_M) \quad [4]$$

By introducing $C_M = \gamma C_S$, and after substitution of $C_{M_1^{2+}}$ from [4] into [2], one obtains:

$$K_{M_2}^{M_1} = \frac{Q_{M_2}(L_{M_1CO_3})^{1/2}}{(Q_{M_1})^{1/2} C_o (C_o - \gamma C_S)} \quad [5]$$

As follows from eqn [5], at constant C_o, C_S and $L_{M_1CO_3}$, $K_{M_2}^{M_1}$ increases with γ and may reach sufficiently high value ($\gg 1$), as $\gamma \to C_o/C_S$. Equation [5] can be rewritten in a more general form for the displacement of the divalent metal ion from the resin with an IXISS-active stripping agent bearing a monovalent counterion as follows:

$$K_{Sss}^{Dis} = \frac{Q_{Dis} L_{Sss}^{1/2}}{(Q_{Sss})^{1/2} C_o (C_o - \gamma C_S)} \quad [6]$$

Here 'Dis' and 'Sss' superscript and subscript denote the displacer and the substance under supersaturation (the product), respectively; C_o is the concentration of the displacer solution, L is the solubility product of the target compound, C_S is the solubility of the product at a given temperature, and γ is the degree of supersaturation for the product solution. Relationship [6] is the fundamental equation describing the shift of IE equilibrium in IXISS systems of different types.

2. The successful application of the IXISS effect requires, on the one hand, maximum stability of the SS in the interstitial space of the column during the IE treatment cycle and, on the other hand, fast decomposition (crystallization) of this solution after its removal from the column. In the case of inorganic substances a unified interpretation of the IXISS phenomenon must be based on general principles of the aggregative stability of dispersion systems, adapted to the particular IE system.
3. The following main factors may influence the stability of dispersions of precrystalline molecular aggregates in the interstitial space of a column: firstly, an effective charge of the polymolecular aggregate (micelle), which is due to the sorption of either counter- or co-ions on the particle surface; and secondly, the ionic strength of the medium, which may strongly influence the coagulation (crystallization) conditions. If, for example, an excess of co-ions exists in the interstitial space, the charge of the micelles will be the same as that of the functional groups of the ion exchanger. In this case, the sorption of the micelles on the surface of the ion exchanger beads becomes impossible and a stabilizing action of the resin bed towards SS can be expected. In contrast, in the presence of an excess of counterions, the charge sign of the precrystalline aggregates will be opposite to that of the functional groups and fast decomposition of SS must be observed due to the sorption of micelles on the surface of the ion exchanger, followed by crystallization of the component under supersaturation.

Manufacture of Chlorine-free Potassium Fertilizers[2]

The production of chlorine-free potassium salts (with minimum Cl^- admixture) such as K_2SO_4, and others, is of particular interest since it deals with the problem

[2] Adapted with permission from Muraviev D, Khamizov R, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. I. Synthesis of chlorine-free potassium fertilizers by an ion-exchange isothermal supersaturation technique. *Industrial Engineering and Chemistry Research* 37: 1950–1955.

of effectively cultivating some chlorophobic plants (e.g. citruses, vegetables and herbs) which are adversely affected by high Cl^- concentration. Potassium sulfate is produced in substantial quantities in Europe by the Mannheim process from K_2CO_3 and H_2SO_4 or by reaction of H_2SO_4 with KCl. Both versions of the Mannheim process are complicated by problems of utilizing gaseous wastes (CO_2 and HCl). In the USA and some other countries, K_2SO_4 is manufactured by exchange reactions between potassium, sodium and magnesium salts by their dissolution and fractional crystallization. This latter process requires utilization of large volumes of liquid waste. The IE synthesis of K_2SO_4 from KCl and $Na_2SO_4 \cdot 10H_2O$ is based either on cation or anion exchange reactions:

Cation exchange synthesis

$$\text{R-SO}_3\text{Na} + \text{KCl} \Rightarrow \text{R-SO}_3\text{K} + \text{NaCl} \qquad [7]$$

$$2\text{R-SO}_3\text{K} + \text{Na}_2\text{SO}_4 \Rightarrow 2\text{R-SO}_3\text{Na} + \text{K}_2\text{SO}_4\downarrow \qquad [8]$$

Anion exchange synthesis

$$\text{R-N(CH}_3)_3\text{Cl} + \text{Na}_2\text{SO}_4 \Rightarrow (\text{R-N(CH}_3)_3)_2\text{SO}_4 + 2\text{NaCl} \qquad [9]$$

$$(\text{R-N(CH}_3)_3)_2\text{SO}_4 + 2\text{KCl} \Rightarrow 2\text{R-N(CH}_3)_3\text{Cl} + \text{K}_2\text{SO}_4\downarrow \qquad [10]$$

In the first process, a sulfonate cation exchanger is first converted from the Na^+ into the K^+ form with dilute KCl solution (0.1 mol dm^{-3}), followed by desorption (stripping) of the product (K_2SO_4) with concentrated Na_2SO_4 solution (2 mol dm^{-3}). The second process starts with the conversion of a strong base anion exchanger from the Cl^- into the SO_4^{2-} form with dilute Na_2SO_4 solution ($\sim$0.25 mol dm^{-3}). K_2SO_4 is then produced during the stripping of sulfate ions with concentrated KCl solution ($\sim$3–4 mol dm^{-3}). The stripping of K_2SO_4 from the resins in both cases leads to the formation of an SS of K_2SO_4 with a degree of supersaturation, γ, of approximately 2. Nevertheless, K_2SO_4 does not precipitate in the column and remains as a stable SS at least for a period of several hours. At the same time, this SS crystallizes spontaneously following its removal from the column. The maximum efficiency of the first process (see eqns [7] and [8]) is achieved when the stripping of the product is carried out at 308 K, followed by crystallization of K_2SO_4 at 293 K to provide the highest difference in sodium and potassium sulfate solubilities inside the column. The second process (see eqns [9] and [10]) appears to be more efficient when carried out at 282 K to minimize the solubility of K_2SO_4 in the solution collected.

The IE equilibrium in both systems is shifted to the right when using dilute KCl and Na_2SO_4 solutions at the first stages of both processes. Application of IXISS effect in the flowsheets of both processes allows the product formation stage to be improved due to the shift of IE equilibrium in reactions 8 and 10 to the right. This clearly follows from eqn [5], which can be rewritten for, e.g. SO_4^{2-}–Cl^- exchange (see reaction [9]), in terms of the equilibrium separation factor α (usually written using either equivalent or equivalent fraction concentration scales):

$$\alpha_{SO_4}^{Cl} = \frac{q_{Cl}}{q_{SO_4}} \frac{K_D \gamma C_S}{C_o(C_o - \gamma C_S)} \qquad [11]$$

Here K_D is the dissociation constant of K_2SO_4. The same reasoning is applicable to interpret the selectivity reversal in the cation exchange system.

Another advantage of the IXISS-based synthesis of K_2SO_4 deals with the possibility of reusing the supernatants obtained after crystallization of K_2SO_4 as a displacer in the subsequent stripping cycles. For example, after separation of K_2SO_4 crystals, the supernatant obtained in the first process is fortified with Na_2SO_4 up to the desired concentration of sulfate ions (2 mol dm^{-3}) and is then directed to the next stripping cycle. A diagram of the cation exchange version of the process for the synthesis of chlorine-free potassium sulfate is given in **Figure 1.** The unit comprises two ion exchange columns operating intermittently in a loading (see eqn [7]) or displacement (see eqn [8]) mode of operation. The second stage (displacement) is carried out using an Na_2SO_4 (or a Na_2SO_4–K_2SO_4 mixture) solution at 308 K. The rinsing water produced after each stage is returned to the process and is used to dissolve either KCl (rinsing after loading) or Na_2SO_4 (rinsing after displacement). The NaCl effluent obtained after the loading stage is directed into the reverse osmosis unit, which produces desalinated water and NaCl concentrate, used to manufacture crystalline NaCl. The desalinated water obtained is returned to the process. Hence, the process is essentially wasteless and ecologically clean.

Decalcination of Mineralized Waters

A number of modern technologies include water treatment processes, which in many instances involve a calcium removal stage. IE methods are widely applied to solve this problem for low mineralized surface waters. The problem of processing highly

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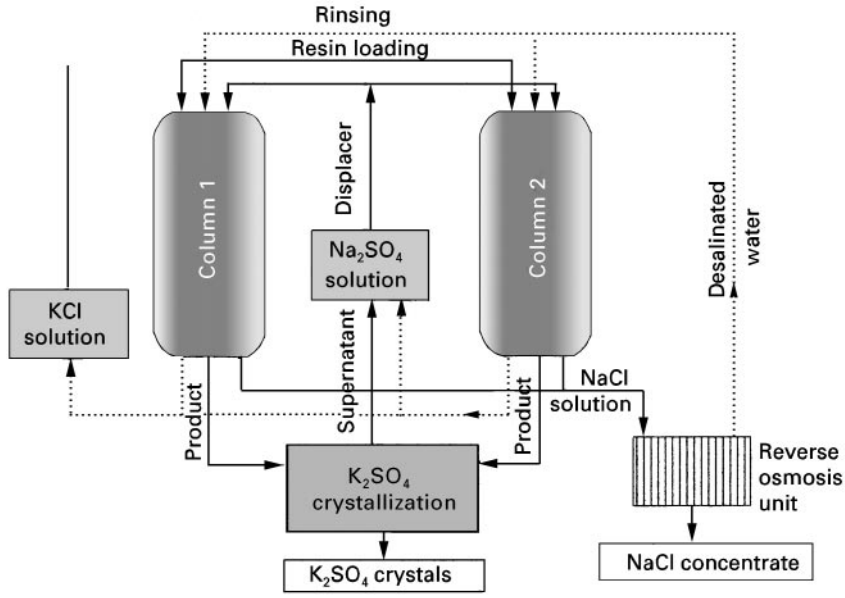

Figure 1 Flowsheet of process for cation exchange synthesis of chlorine-free potassium sulfate. (Reproduced from Muraviev D, Khamizov R, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. I. Synthesis of chlorine-free potassium fertilizers by an ion-exchange isothermal supersaturation technique. *Ind. Eng. Chem. Res.* 37: 1950–1955, with permission from the American Chemical Society.

mineralized waters is far more complicated. For example, preliminary treatment of seawater prior to its further desalination requires extensive decalcination to solve the problem of gypsum formation on heater surfaces of distillers and clogging of membranes in reverse osmosis or electrodialysis units. Modern seawater-processing technologies, such as IE recovery of magnesium, also require preliminary removal of calcium.

The problem of calcium removal from seawater (and highly mineralized waters and brines) can be successfully solved by using an IXISS-based process on specially modified conventional (low cost) sorbents with enhanced selectivity for Ca^{2+}. The first requirement is dictated by the necessity for the efficient use of the sorbent capacity towards Ca^{2+} at $\sim$ five-fold magnesium over calcium excess in the seawater under treatment. The second arises from the need to process 1000 m^3 of seawater to produce 1 ton of magnesium. For example, several successive treatments of zeolites (e.g. of A type) with seawater and a concentrated NaCl solution result in their stable modification due to irreversible sorption of Mg^{2+}. An average α_{Mg}^{Ca} value for the modified zeolite (from seawater) rises to ~ 27 in comparison with 4.5 for the unmodified sorbent. The sorbent removes virtually no Mg^{2+} from seawater, whereas Ca^{2+} uptake appears to be nearly equal to its capacity ($\sim$4 mmol kg^{-1}). At the same time, α_{Na}^{Ca} for the modified zeolite remains at a sufficiently low level ($\sim$3.6) to simplify its regeneration with sodium salt solutions after the loading with Ca^{2+}. The most efficient desorption of Ca^{2+} from zeolite is achieved by using an $NaCl$–Na_2SO_4 mixture. The reaction of Ca^{2+}–Na^{+} exchange is coupled in this case with the reaction of $CaSO_4$ formation and, as a result, the equilibrium in the system is shifted to the right. The overall desorption process is described by the following equation:

$$\left(x + \frac{y}{2}\right)\mathrm{R_2\text{-}Ca} + x\mathrm{Na_2SO_4} + y\mathrm{NaCl} = (2x + y)\mathrm{R\text{-}Na} + x\mathrm{CaSO_4}\downarrow + \frac{y}{2}\mathrm{CaCl_2} \qquad [12]$$

The optimal molar ratio of Na_2SO_4 to NaCl (x/y in eqn [12]) in the regenerating solution is 0.2. In this case the regeneration of zeolite requires a close to stoichiometric amount of the regenerating agent. The eluate obtained during the stripping stage (**Figure 2**) is supersaturated ($\gamma \approx 5$). Nevertheless, it coexists with the granulated sorbent phase for a long period ($\sim$24 h at 293 K) as a stable SS. This solution spontaneously crystallizes following removal from the column with the formation of gypsum, which is the only waste product in the process. After removal of the $CaSO_4$ precipitate by filtration, the supernatant can be fortified with the desired amount of $NaCl$–Na_2SO_4 mixture and returned to the process for reuse. The process is carried out in a two-fixed bed column set-up. The columns operate intermittently in a calcium removal and regeneration mode.

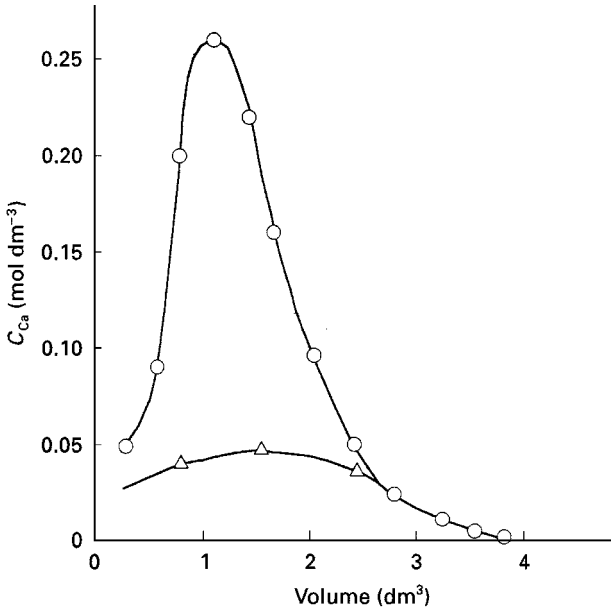

Figure 2 Desorption of Ca^{2+} from modified zeolite A with 1.25 mol L^{-1} NaCl + 0.25 mol L^{-1} Na_2SO_4 mixture (circles). Triangles, calcium concentration in supernatant after crystallization of supersaturated solution samples. (Modified with permission from Muraviev *et al.*, 1998).

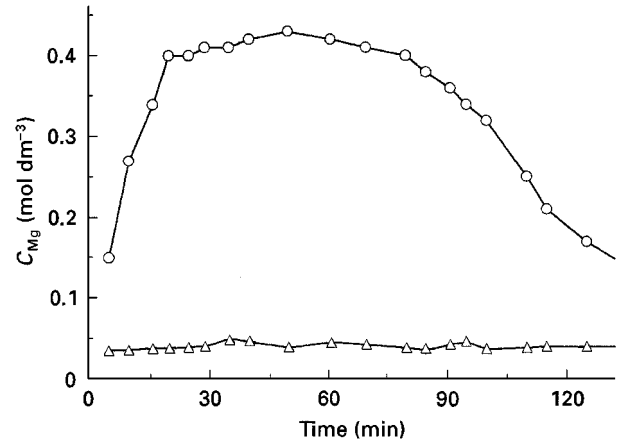

Figure 3 Concentration–time history of desorption of Mg^{2+} with 1.5 mol L^{-1} Na_2CO_3 + 0.60 mol L^{-1} $NaHCO_3$ (circles) from carboxylic resin pre-loaded with decalcinated natural seawater at 293 K. Triangles, Mg^{2+} concentration in supernatant after short-term heating (during 10 min from 290 to 310 K) followed by crystallization of supersaturated solution samples. (Reproduced from Khamizov R, Muraviev D, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. II. Recovery of high-purity magnesium compounds from seawater by an ion-exchange, isothermal supersaturation technique. *Ind. Eng. Chem. Res.* 37: 2496–2501, with permission from the American Chemical Society.

Recovery of High Purity Magnesium Compounds from Seawater[3]

The traditional magnesium-from-seawater technology includes mixing the raw seawater with 'milk of lime' filtration of $Mg(OH)_2$ slurry, followed by its treatment with HCl, evaporation, drying and electrolysis. The process does not allow for producing sufficiently pure Mg. The possibility of designing an alternative IXISS-based process for recovery of high purity Mg compounds from seawater has appeared from the discovery of IXISS of $MgCO_3$ in the resin bed. The IXISS effect is observed during elution of Mg^{2+} from carboxylic resin pre-loaded with decalcinated seawater with a solution of Na_2CO_3–$NaHCO_3$ mixture. Magnesium carbonate does not precipitate in the column and remains as a stable SS (with $\gamma \approx 5$) at least over a period of 72 h. After removal of this solution from the column (**Figure 3**), the desorbed magnesium spontaneously crystallizes in the form of well-shaped nesquegonite ($MgCO_3$ $3H_2O$) crystals. The purity of magnesium compound obtained appears to be $> 99.9\%$ since, unlike magnesite ($MgCO_3$), nesquegonite crystals are calcium-free. The yield of $MgCO_3$ $3H_2O$ depends on the conditions of crystallization of the SS collected. Thus, crystallization at ambient temperature over several hours gives $\sim 70\%$ yield of the product in one desorption cycle. A rapid increase of temperature in the crystallizer from ~ 290 K to ~ 310 K over 10 min) allows for a substantial increase in the rate of crystallization, which results in the rise of the product yield to $> 90\%$.

The block scheme of the pilot unit for recovery of high purity $MgCO_3$ from seawater is shown in **Figure 4**. Ca-free seawater (see previous section) passes from the top to the bottom through two of the three columns C_1–C_3, loaded with carboxylic resin in the Na form. At the same time the third column is working in the regeneration (magnesium-stripping) mode of operation. After conversion of resin in the Mg form the columns are treated from the bottom to the top with a stripping solution of 1.5 mol L^{-1} Na_2CO_3 + 0.6 mol L^{-1} $NaHCO_3$ mixture (also containing a residual $MgCO_3$ from the recycled stripping solution). Ca-free seawater, displaced from the columns, is directed to tank T_1 until the appearance of supersaturated eluate which, in turn, is directed to tanks T_2 and T_3 (crystallizers supplied with heating and filtration facilities to collect the crystalline product) by reswitching the automatic valve V_1. After crystallization and removal of magnesium carbonate,

[3] Adapted with permission from Muraviev D, Khamizov R, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. II. Recovery of high-purity magnesium compounds from seawater by an ion-exchange isothermal supersaturation technique. *Industrial Engineering and Chemistry Research* 37: 2496–2501.

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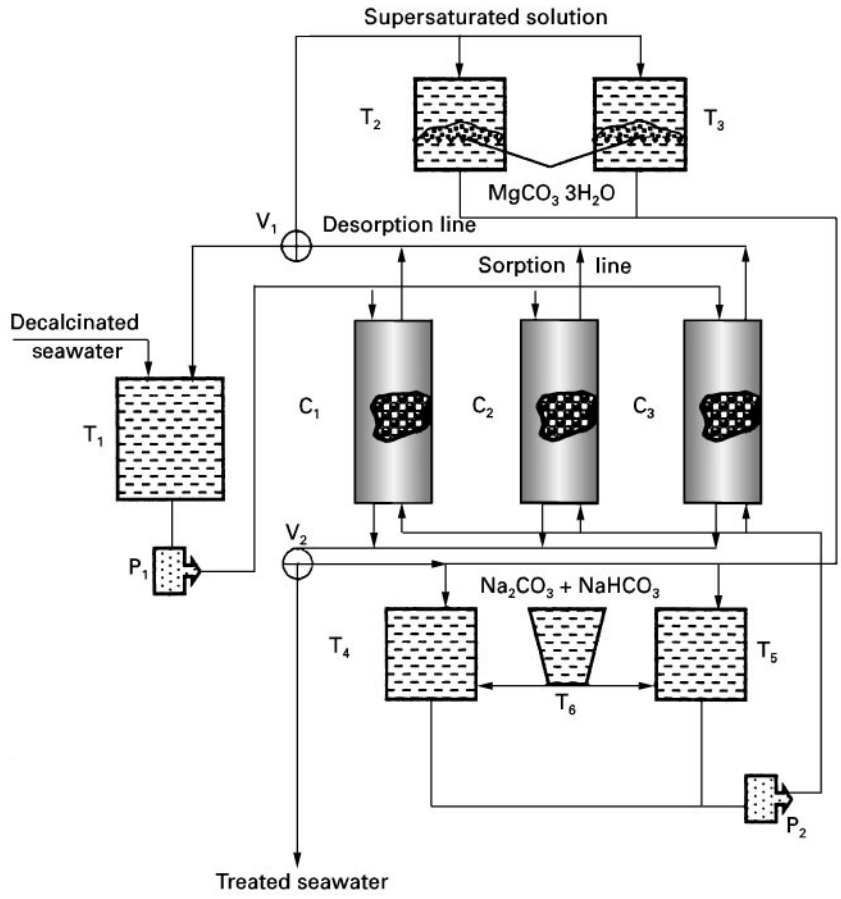

Figure 4 Schematic diagram of experimental pilot unit for recovery of high purity magnesium compounds from seawater: ion exchange columns C_1–C_3; solution tanks T_1–T_6; solution pumps P_1 and P_2; automatic valves V_1 and V_2. (Reproduced from Khamizov R, Muraviev D, Tikhonov N *et al.* (1998). Clean ion-exchange technologies. II. Recovery of high-purity magnesium compounds from seawater by an ion-exchange isothermal supersaturation technique. *Ind. Eng. Chem. Res.* 37: 2496–2501, with permission from the American Chemical Society.

the stripping solution is returned to tanks T_4 and T_5 for fortification with the desired amount of the Na_2CO_3–$NaHCO_3$ mixture from T_6 and reuse. Then the sorption cycle is repeated. The stripping solution displaced from the columns is also returned to T_4 and T_5 until the appearance of treated seawater in the line that is controlled by the automatic valve V_2. Hence, the process shown in Figure 4 is totally free of waste.

Dual-temperature IE Processes

The efficiency of the dual-temperature IE process is primarily determined by the temperature sensitivity of the IE system which, in turn, depends on the value of the heat effect of a given IE reaction. The thermodynamics of a reversible IE reaction in the system including, for example, counterions A^{z_A+} and B^{z_B+}, a co-ion X^{z_X-} and a cation exchanger R bearing univalent functional groups can be described by the Gibbs–Helmholtz equation:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad [13]$$

and the isotherm of an IE reaction by:

$$\Delta G_{P,T} = \Delta G^o_T + RT \ln\left(\frac{a_{AR}^{-1/z_A} a_{BX}^{1/z_B z_X}}{a_{BR}^{-1/z_B} a_{AX}^{1/z_A z_X}}\right) \qquad [14]$$

where $\Delta G^o = -RT \ln K$, and K is the thermodynamic equilibrium constant of the IE reaction corresponding to the condition $\Delta G_{P,T} = 0$.

Eqns [13] and [14] lead to the van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \qquad [15]$$

Under standard conditions (when K depends only on temperature), eqn [15] can be rewritten in conventional derivatives and then integrated from T_1 to T_2.

In the simplest case, when ΔH is independent of temperature, one obtains:

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad [16]$$

The resulting relationship [16] is widely used to describe dual-temperature IE processes.

Concentration of Magnesium and Bromine from Seawater

At present, around 25% of overall world production of magnesium and 70% of that of bromine is provided from the sea and other hydromineral resources. Traditional methods for producing Mg (see previous section) and Br (air-stripping technique) by processing seawater, despite their profitability, do not satisfy increasingly stringent ecological standards. Consequently, new alternative ecologically clean technologies, based on IE separation methods, have to be developed. The dual-temperature IE concentration of Mg and Br from seawater is based on the strong temperature dependence of the separation coefficients α_{Na}^{Mg} and α_{Cl}^{Br} of weak acid (for Mg) and strong base (for Br) IE resins, respectively. For example, the α_{Cl}^{Br} value decreases by a factor of ~ 2, while α_{Na}^{Mg} value increases by a factor of ~ 1.2 when the temperature of seawater rises from 283 to 363 K. The principle of the dual-temperature concentration of Mg and Br by using a cascade of fixed-bed columns is shown in Figure 5. The first column is intermittently treated with hot and cold seawater depending on the mode of operation, e.g. thermosorption or thermostripping. Respective concentration–volume histories are shown in **Figure 6** for the Mg concentration process. The resulting eluate is either collected in tank Conc. 1 (Mg or Br concentrate after thermostripping) or returned to the sea (after thermosorption). The concentrate obtained after the first column is subjected to the same sequence of operations on the second column to produce the second concentrate, and so forth.

In a subsequent treatment of cold and hot seawater in a fixed-bed IE column, the concentration of Br^- in the hot stripping solution increases by a factor of 2, while the concentration of Cl^- and SO_4^{2-} decreases. The multistage process (using AV-17 anion exchange resin, Reakhim, Moscow, Russia, Russian analogue of strong base anion exchangers such as, e.g. Dowex-1, Amberlite IRA 400, Purolite A 400 and Lewatit M 500) enriches Br^- concentration in the final concentrate up to an acceptable level for further processing (> 5 g L^{-1}). Four dual-temperature sorption-stripping cycles (using Lewatit R 250 K resin, Bayer, Germany) allow for concentrating Mg up to ~ 0.4 mol dm^{-3} (versus 0.11 mol dm^{-3} in the initial seawater), as shown in **Figure 7**. The final concentrate can be decalcinated and used for producing high purity magnesium (see above). The resins used in both processes do not require any regeneration. Hence, the processes are completely free of waste products.

Reduction in energy expenditure for heating the seawater can be successfully solved by using conventional, or concentrated, sunlight (in areas with a high level of solar radiation) as the principle and

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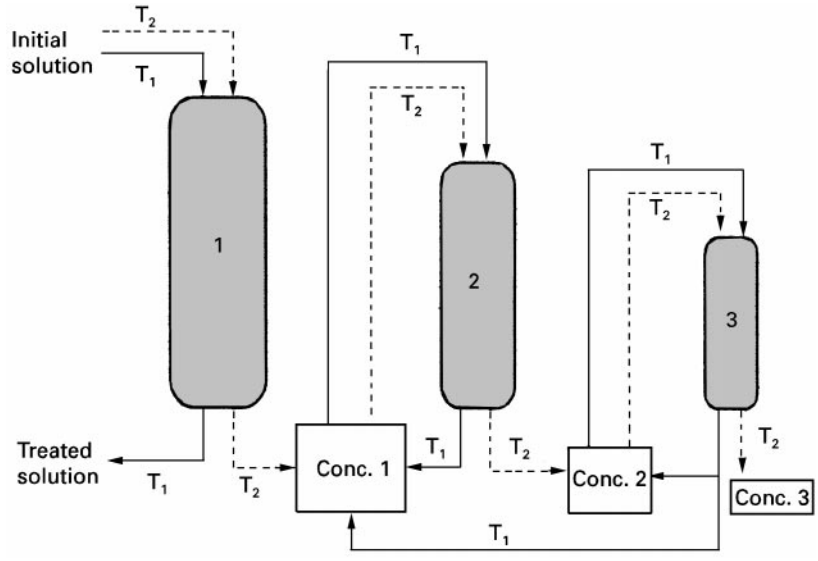

Figure 5 Flowsheet of reagentless dual-temperature ion exchange processing of seawater. (Reproduced from Muraviev D, Noguerol J and Valiente M (1997) Seawater as auxilliary reagent in dual-temperature ion-exchange processing of acidic mine waters. *Environ. Sci. Technol.* 31: 379–383, with permission from the American Chemical Society.

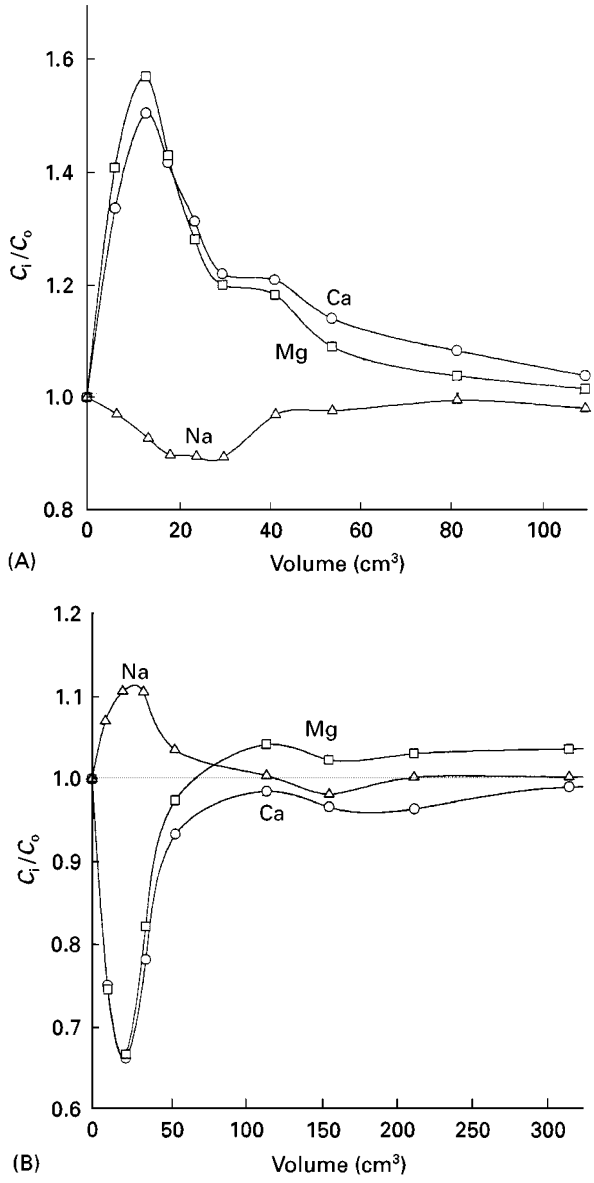

Figure 6 (A) Thermostripping (T = 263 K) and (B) thermosorption (T = 353 K) breakthrough curves obtained from natural seawater (Mediterranean sea) on polyacrylic Lewatit R 250-K resin. Circles, calcium; squares, magnesium; triangles, sodium. (Reproduced from Muraviev D, Noguero J and Valiente M (1996). Separation and concentration of calcium and magnesium from seawater by carboxylic resins with temperature-induced selectivity. *Reactive and Functional Polymers* 28: 111–126, with permission from Elsevier Science.

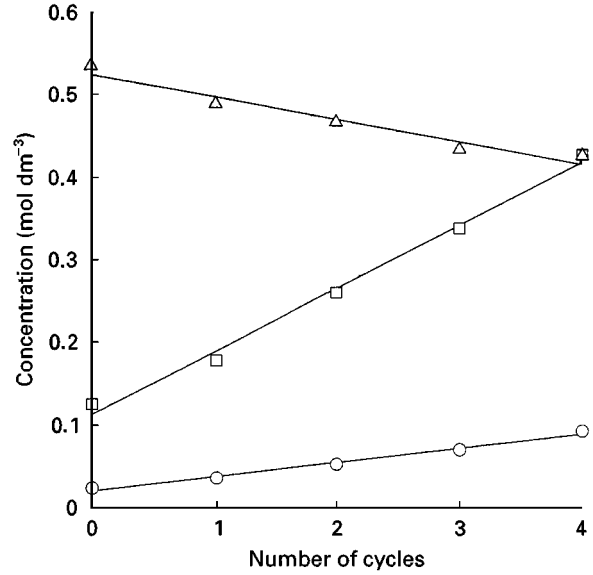

Figure 7 Concentration of Ca^{2+} (circles), Mg^{2+} (squares) and Na^{+} (triangles) obtained in consecutive thermostripping–sorption cycles vs number of cycles. (Reproduced from Muraviev D, Noguerol J and Valiente M (1996) Separation and concentration of calcium and magnesium from seawater by carboxylic resins with temperature-induced selectivity. *Reactive and Functional Polymers* 28: 111–126, with permission from Elsevier Science.

ecologically clean energy source (sun-boiler systems). An alternative solution can be the use of seawater in the cooling cycles of steam power stations. The amount of seawater pumped through the cooling cycles of these stations is approximately 20 000–30 000 $m^3\,h^{-1}$. This hot seawater is currently pumped back into the sea, which means that billions of joules of heat are wasted. This seawater could be used for recovering minerals (e.g. Mg and Br). In this way, the power costs in heating seawater and moving it through the mineral recovery process (which substantially exceeds 50% of the overall expenditures for electricity) could be written off.

Concentration of Copper from Acidic Mine Waters[4]

The treatment of acidic mine waters (AMW), representing natural effluents from pyritic ore deposits, is of great economic and ecological importance. The AMW are characterized by low pH (~2) and relatively high concentrations of metal ions such as Fe^{3+}, Zn^{2+} and Cu^{2+} (**Table 2**). The initial AMW requires pre-conditioning by selective removal of iron prior to IE treatment. This conditioning is carried out by adjusting the pH to 3.4–3.5 with alkali followed by either conventional or biooxidation of Fe(II) to Fe(III). The final removal of the $Fe(OH)_3$ precipitate is carried out by filtration.

Two commercial IE resins, namely a polyacrylic (e.g. Lewatit R 250-K) and an iminodiacetic (e.g.

[4] Adapted with permission from Muraviev D, Noguerol J and Valiente M (1997). Application of the reagentless dual-temperature ion-exchange technique to a selective separation and concentration of copper versus aluminium from acidic mine waters. *Hydrometallurgy* 44: 331–346.

Table 2 Composition of initial and conditioned samples of native acidic mine waters (AMW) from Rio Tinto area (Huelva, Spain)[a]

AMW sample	Concentration *(mg L^{-1})*								*pH*
	SO_4^{2-}	*Fe*	*Cu*	*Zn*	*Al*	*Mn*	*Mg*	*Ca*	
1 (initial)	16 450	5050	239	912	399	75	751	326	1.9
1 (conditioned)	16 300	3	235	890	386	73	735	319	3.5
2 (conditioned)	17 350	0.3	115	1275	530	90	950	475	3.5

[a] The AMW samples have been collected from the natural generic metal-bearing effluents originated from the pyritic ore deposits typical for the southern provinces of Spain and Portugal.

Lewatit TP-207) can be used for the dual-temperature IE concentration of copper from AMW. Acrylic resin is selective for Al^{3+} (over other AMW metal ions) and iminodiacetic resin manifests high selectivity towards Cu^{2+}. The uptake of Al^{3+} increases remarkably while that of Cu^{2+} decreases with temperature for both resins and that for the rest of the metals depends weakly on temperature. This effect gives the possibility for the dual-temperature IE concentration of copper from AMW by using the same set-up and the mode of operation as shown in Figure 5. The resins are first equilibrated with cold AMW (at 293 K). Then a selective thermostripping of Cu^{2+} is carried out using hot AMW (at 353 K), leading to an increase in Cu^{2+} concentration in the eluate by a factor of 1.3 (for acrylic resin) or 1.2 (for iminodiacetic resin). The concentration of Al^{3+} in the same eluate drops to 50% in the first case and to 70% in the second. The efficiency of both thermosorption and thermostripping processes (at constant solution flow rates and resin bed heights) depends on the interval of working temperatures (see eqn [11] and is higher the greater this interval (**Figure 8**).

The concentration of Cu^{2+} achieved after the fourth thermosorption–thermostripping cycle increases (in comparison with the initial AMW) by a factor of $\sim$3, while that of Al^{3+} decreases by one order of magnitude (**Figure 9**). The substantial increase in the efficiency of the process (higher degree of concentration) can be achieved using either higher fixed resin bed columns (see Figure 5) or a cascade of countercurrent columns, as shown in **Figure 10**. The unit comprises several two-section countercurrent columns which are operated at different temperatures to provide thermosorption/ thermostripping conditions in the sections. The first column is fed by the native AMW and produces the first concentrate, which is collected from the boundary between sections and then directed to the bottom section of the second column and so on. The resin in all columns circulates in a closed cycle and does not require regeneration. The unit shown in **Figure 10** can also be used for the dual-temperature IE processing of seawater to produce magnesium or bromine concentrates in a continuous mode of operation.

Concluding Remarks

The number of large scale industrial applications of both dual-temperature IE and IXISS-based IE processes is still very limited. For example, the dual-temperature partial demineralization of surface waters using specially synthesized polyampholyte resins (so-called Sirotherm process) so far remains the only industrial application of dual-temperature IE. At present, a large scale pilot plant using the countercurrent version of an IXISS-based process for the recovery of more than 300 tons of high purity magnesium carbonate from seawater per year has started operation in the Vladivostok region of Russia. The unit shown in Figure 4 adequately imitates the basic flowsheet of Vladivostok plant in the fixed-bed mode of operation.

The prospects for wider implementations of ecologically clean IE processes in different fields of industry are primarily determined by their obvious advantages and relative simplicity. For example, the use of IXISS effect in the design of highly efficient and ecologically safe IE technology does not require any specific IE equipment and can be easily realized using standard IE columns. At the same time, a deeper insight into the IXISS phenomenon can substantially widen the area of practical application of this effect. In this regard, the solution of the following problems seems to be of particular importance:

1. Identification of chemical compounds (both organic and inorganic) exhibiting IXISS effect (IXISS-active compounds)
2. Evaluation of stabilizing efficiency of commercially available IE materials towards SS of IXISS-active compounds of different types (electrolytes, nonelectrolytes, polyampholytes and zwitterlytes)
3. Development of theoretical fundamentals of IXISS effect and some others

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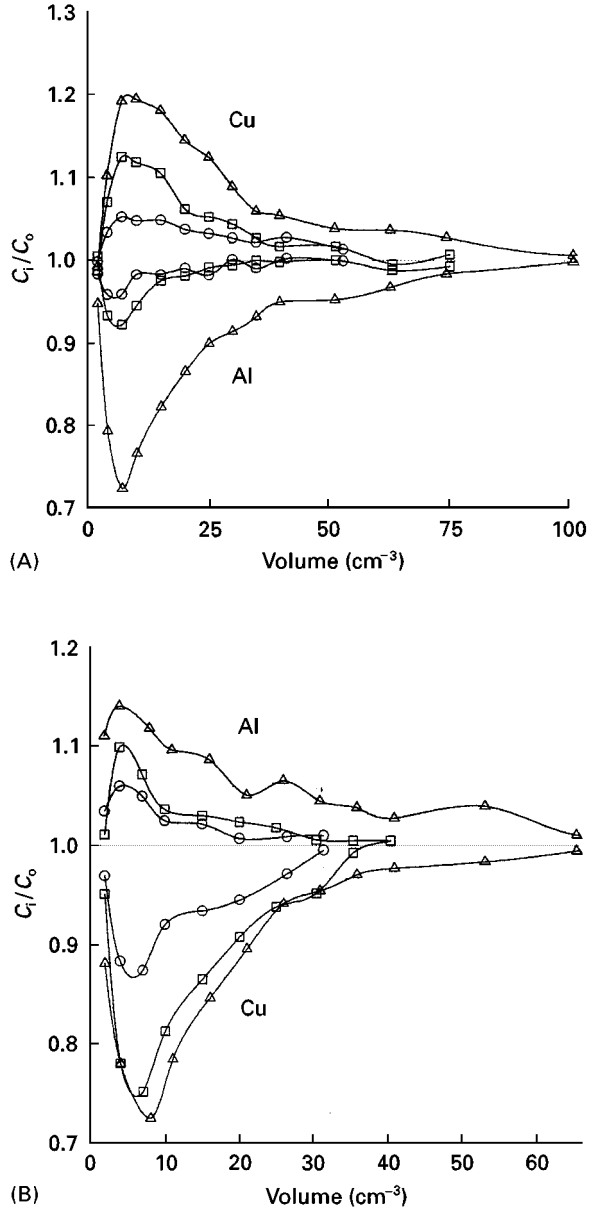

Figure 8 (A) Thermostripping and (B) thermosorption breakthrough curves for Cu^{2+} and Al^{3+} obtained from native AMW (see Table 2) on iminodiacetic Lewatit TP-207 resin at various thermostripping temperatures: 313 K (circles); 333 K (squares); 353 K (triangles). Thermostripping is carried out at indicated temperature after loading of resin at 293 K. Thermosorption is carried out at 293 K after finishing the thermostripping cycle at the indicated temperature. (Reproduced from Muraviev D, Noguerol J and Valiente M (1997) Application of the reagentless dual-temperature ion-exchange technique to a selective separation and concentration of copper versus aluminium from acidic mine waters. *Hydrometallurgy* 44: 331–346, with permission from Elsevier Science.

Several recent publications and reviews by the author are recommended to those interested in this subject.

Unlike IXISS-based IE processes, large scale industrial applications of dual-temperature IE requires in certain instances the design of special IE equipment such as, for example, two-sectional jacketed IE columns providing the dual-temperature mode of operation. At the same time, it seems useful to emphasize that the shift of chemical equilibrium to the desired direction due to the modulation of temperature in the system represents one of the basic physicochemical concepts which are widely used in different fields of chemical technology. From this viewpoint the dual-temperature IE cannot be considered as a somewhat exotic separation method as in many instances the experience (both theoretical and experimental) accumulated in other areas of chemical science and engineering can be successfully applied for the further development of this fractionation technique. On the other hand, it seems useful to distinguish the following problems, the solution of which can help to widen the application of dual-temperature IE in industry:

1. the evaluation of temperature sensitivity of commercially available ion exchangers towards different ionic systems of practical interest to estimate their potential use in dual-temperature IE processes
2. the tailored design and synthesis of temperature-responsive IE resins tuned for the dual-temperature IE fractionation of certain ion mixtures. Ion exchangers of this type are not so far commercially

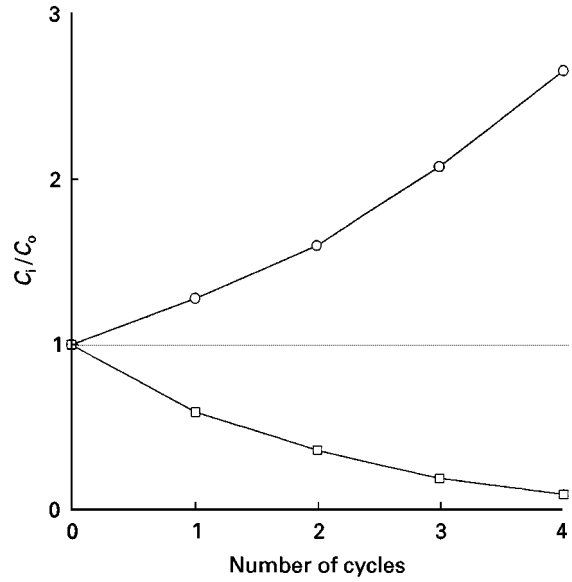

Figure 9 Concentrations of Cu (circles) and Al (squares) obtained in consecutive thermosorption–stripping cycles from AMW on iminodiacetic Lewatit TP-207 resin vs number of cycles. (Reproduced from Muraviev D, Noguerol J and Valiente M (1997) Application of the reagentless dual-temperature ion-exchange technique to a selective separation and concentration of copper versus aluminium from acidic mine waters. *Hydrometallurgy* 44: 331–346, with permission from Elsevier Science.

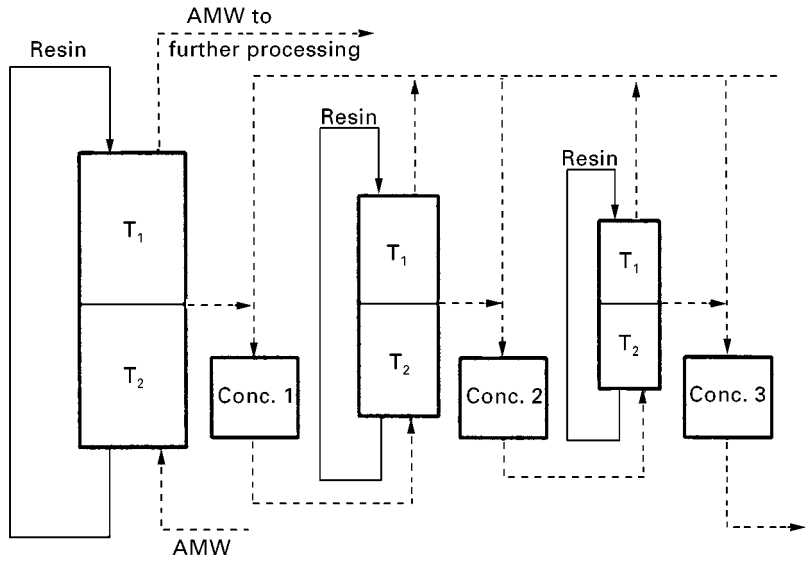

Figure 10 Flowsheet of continuous process for dual-temperature ion exchange treatment of acidic mine waters. (Reproduced from Muraviev D, Noguerol J and Valiente M (1997) Application of the reagentless dual-temperature ion-exchange technique to a selective separation and concentration of copper versus aluminium from acidic mine waters. *Hydrometallurgy* 44: 331–346, with permission from Elsevier Science.

available. Their appearance can dramatically stimulate the further development and wider application of dual-temperature IE techniques

3. the combination of dual-temperature-based and conventional IE processes within one technological flowsheet will increase the efficiency of the whole process

Interested readers can find more detail on the subject in the recent review by Muraviev *et al*.

See also: **II/Ion Exchange:** Organic Ion Exchangers; Historical Development; Theory of Ion Exchange.

Further Reading

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